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On the Crystal Structure of the Manganese (III) Trioxides of the Heavy Lanthanides and Yttrium*

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The preparation, determination of optical properties, and approximate crystal structure of the ferroelectric manganese (III) trioxides of holmium, erbium, thulium, ytterbium, lutetium, and yttrium are reported. The compounds crystallize in the hexagonal system, probable space group $P6_3cm$, and their structure is characterized by unusual five- and sevenfold coordination polyhedra about manganese and rare-earth atoms respectively. The unacceptable values assumed by the temperature factors of two oxygen ions throw doubt on the exact determination of atom positions by least-squares refinement. Possible causes of this difficulty are reviewed.

Introduction

Perovskite- or distorted perovskite-type structures have been ascribed to ABO_3 compounds where B is a trivalent manganese ion and A is a trivalent rare-earth ion of the set La^{3+} (Yakel, 1955), Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+} (Bertaut & Forrat, 1956), Dy^{3+} (Vickery & Klann, 1957), Y^{3+} (Forrat, 1958), and Tb^{3+} (Bertaut & Koehler, 1959) (*cf.* Vickery & Klann, 1957, for Pr^{3+} and Nd^{3+}; Forrat, 1958, for Dy^{3+}; and Belov, Zaitseva & Pedko, 1959, for Gd^{3+}). As the radii of the trivalent cations of the heavier rare-earth elements decrease, one may suspect their manganese (III) trioxides would adopt some new crystal structure in which the smaller ions would be better accommodated than in a perovskite-like structure (Goldschmidt, 1926*a*, *b*).

The purpose of this paper is to describe briefly the preparation of the compounds $HoMnO_3$, $ErMnO_3$, $TmMnO_3$, $YbMnO_3$, $LuMnO_3$, and $YMnO_3$, and to present the results of an approximate determination of the crystal structure common to these compounds.

Compound formation and crystal growth

Manganese (III) trioxides of Ho, Er, Tm, Yb, Lu, and Y were prepared by dissolving stoichiometric quantities of the rare-earth oxide and metallic manganese in nitric acid, evaporating the solutions to dryness with an infrared lamp, prefiring at about 200 °C to drive off volatile residues, and then igniting in air at about 1100 °C. The erbium and lutetium compounds were also formed by firing mixtures of the rare-earth oxides and MnO_2 in air at about 1100 °C.

Visual examination of the reaction products showed them to be microcrystalline, blackish-red powders with no apparent inhomogeneities. Chemical analyses indicated the formula $AMnO_3$ (A = rare earth). The oxidation power of these materials was consistent with the assignment of the 3^+ oxidation state to all of the manganese present. The chemical method could not distinguish between 100% Mn^{3+} and 50% Mn^{2+}–50% Mn^{4+}, but since subsequent structure analyses could find only one crystallographically distinct manganese atom per asymmetric unit, the latter is considered improbable. The density of the $ErMnO_3$ compound was found pycnometrically to be $7{\cdot}20 \pm 0{\cdot}03$ g.cm^{-3}.

Apparent single crystals of these compounds were grown by heating oxide mixtures with equivalent A:Mn cation ratios at 1200 °C for about 48 hr in a bismuth oxide flux (12:1 molar ratio of Bi_2O_3:A_2O_3), then slowly cooling the mixtures to room temperature over a period of 12–24 hr. The crystals produced had a plate-like habit (0·1–0·5 mm average linear dimension in the plane of the plate), but one experiment with $LuMnO_3$ produced large (0·1 to 1 mm average linear dimension), well-formed, hexagonal dipyramids truncated by basal pinacoids. In the case of $YMnO_3$, two distinct and separable crystal habits were observed, one plate-like, the other more prismatic.

Lath-like $LuMnO_3$ crystal fragments were dichroic in plane polarized light and birefringent under crossed Nicols, with extinctions parallel and perpendicular to the long direction of the lath. The color of the crystals in plane polarized light changed from reddish black (vibration vector parallel to the long direction of the lath) to light green (vibration vector normal to

* A preliminary report of the crystal structure was given at the Fifth International Congress of the International Union of Crystallography, Cambridge, England, August 15–24, 1960 (see Abstract No. 5·8).

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the long direction of the lath). Refractive indices of $1{\cdot}89 \pm 0{\cdot}02$ and $2{\cdot}01 \pm 0{\cdot}02$ were measured parallel and normal to the long direction of the lath respectively. An interference figure could not be observed since no fragment was found which could be viewed parallel to the unique axis. While the morphology of the lath-like crystals is uncertain, it seems probable that their long direction ($\eta_1 = 1{\cdot}89$, red transmission of plane polarized light) corresponds to the z direction of the hexagonal lattice, and that they are therefore uniaxial negative.

The dipyramidal crystals of $LuMnO_3$ gave a positive result when tested for pyroelectricity by a liquid air method (Wooster, 1957). Positive piezoelectric effects were also observed in polycrystalline samples of other compounds in this series. A description of the ferroelectrical properties of the compounds will be found in a following paper (Bertaut, Forrat & Fang, 1963). It may be noted here that the prismatic form* of $YMnO_3$ does not possess ferroelectric properties at room temperature.

X-ray diffraction examination

Reflections appearing on Cu $K\alpha$ ($\lambda = 1{\cdot}5418$ Å) and Fe $K\alpha$ ($\lambda = 1{\cdot}9373$ Å) Debye–Scherrer photographs of powdered $ErMnO_3$ were indexed on the basis of a hexagonal unit cell with $a_0 = 6{\cdot}115$, $c_0 = 11{\cdot}41$ Å, and $c/a = 1{\cdot}8660$. These cell constants, combined with the experimentally observed density, gave a value of $Z = 5{\cdot}94$ formula weights per cell. With $Z = 6$, the theoretical X-ray density is 7·282 g.cm^{-3}. Lattice parameters of the other isomorphous manganese (III) trioxides are given in Table 1. Spacings and indices of a powder diagram of $ErMnO_3$ are listed in Table 2.

The only systematic absences noted in the powder photographs occurred for reflections $h0\bar{h}l$ with $l = 2n+1$. It was also found that all reflections with l odd were weak, and that only reflections with $h-k = 3n$ (except for those subject to the systematic extinction) had observable intensities for $l = 0$ or $l = 2n+1$.

Single-crystal X-ray diffraction studies of $ErMnO_3$, $LuMnO_3$, and $YMnO_3$ (plate-like crystals) confirmed the powder data concerning crystal system, unit cell parameters, and systematic and nonsystematic absences. Combined with goniometric measurements, they also demonstrated that the dipyramidal $LuMnO_3$ crystals were first order, with pyramidal faces of the form $(10\bar{1}1)$, and that the large faces of the plate-like crystals were basal pinacoids.

The diffraction symbol $6/mmm$, $P.c.$ was indicated by the single-crystal data. Further electrical measurements (Bertaut *et al.*, 1963) showed the polar direction to be parallel to z, so that the space group $P6_3cm$ (C_{6v}^3) could be assigned. However, because of their ferroelectric properties, it is probable that even the smallest crystal fragment will contain domains in which the polar direction has opposite orientations. If a lattice rotation should accompany the change in polarity, the collection of domains might give a single-crystal

Table 1. *Unit cell parameters of several hexagonal rare-earth orthomanganites of the* $LuMnO_3$ *type*

Compound	a_0 (Å)	c_0 (Å)	c/a
$YMnO_3$	6·125*	11·41*	1·862*
$HoMnO_3$	6·136	11·42	1·861
$ErMnO_3$	6·115	11·41	1·866
$TmMnO_3$	6·062	11·40	1·881
$YbMnO_3$	6·062	11·40	1·881
$LuMnO_3$	6·042	11·37	1·882

* All a_0 values are $\pm 0{\cdot}001$ Å; c_0 values are $\pm 0{\cdot}01$ Å; c/a values are $\pm 0{\cdot}002$.

* Powder photographs of crushed prismatic $YMnO_3$ crystals are identical with those of the orthorhombic phase (Forrat, 1958) of $YMnO_3$ crystallizing in space group $Pbnm$ with $a_0 = 5{\cdot}32$, $b_0 = 5{\cdot}51$, $c_0 = 7{\cdot}66$ Å.

Table 2. $ErMnO_3$

(Fe $K\alpha$ radiation, $\lambda = 1{\cdot}9373$ Å)

h	k	l	I	d_o	d_c
0	0	2	m	5·567	5·704
1	0	2	w	3·833	3·880
1	1	0	$m+$	3·039	3·056
1	1	1	m	2·937	2·952
0	0	4	m	2·837	2·852
1	1	2	s	2·682	2·685
1	0	4	w	2·497	2·511
2	0	2	vw	2·390	2·401
1	1	4	s	2·079	2·085
2	0	4	m	1·936	1·940
2	1	2	w	1·883	1·888
1	1	5	w	1·823	1·828
1	0	6	w	1·784	1·729
3	0	0	s	1·759	1·764
3	0	2	$m+$	1·682	1·686
2	1	4	w	1·634	1·638
1	1	6	s	1·610	1·614
2	0	6	w	1·541	1·544
2	2	0	w	1·526	1·528
3	0	4	s	1·498	1·500
2	2	2	s	1·473	1·476
0	0	8	vw		1·426
3	1	2	vw		1·422
2	1	6	s	1·377	1·378
2	2	4	s	1·347	1·349
1	3	4	w	1·304	1·305
1	1	8	$m+$	1·291	1·292
2	0	8	m	1·254	1·255
2	2	6	s	1·190	1·191
1	3	6	s	1·161	1·162
1	4	0	$m+$	1·154	1·155
1	4	2	s	1·132	1·132
1	0	10	m	1·115	1·115
3	0	8	m	1·109	1·109
4	0	6	w	1·086	1·086
1	4	4	s	1·070	1·070
2	0	10	w	1·047	1·047
2	2	8	w	1·042	1·042
3	2	6	s	1·023	1·023
3	1	8			
3	3	0	s	1·019	1·019
3	3	2	m	1·003	1·003
2	1	10	$m+$	0·991	0·991
4	1	6	s	0·987	0·987

s: strong; m: medium; $m+$: medium plus; w: weak; vw: very weak.

diffraction pattern with higher apparent symmetry than that possessed by an individual domain. The possibility of pseudosymmetry in the intensity distribution, apart from that which might be due to the domain structure, was not eliminated. Patterns were searched for differences in intensity between reflections *hkil* and *hikl* but no significant variations were found. Despite this negative result, $P3c1$ (C_{3v}^3) was considered a possible space group.

Reflection intensity data were collected from a fragment of a crushed dipyramidal $LuMnO_3$ crystal. Mo $K\alpha$ ($\lambda=0{\cdot}7107$ Å) radiation and a Weissenberg goniometer, with Geiger counter (xenon-filled) attachment, were used in equi-inclination geometry. The crystal was approximately rod shaped; its length was 0·01 cm and its average diameter was 0·002 cm. The z axis of the hexagonal unit cell was parallel to the long dimension of the crystal, which was aligned parallel to the rotation axis. Of the 1548 independent* reflections, not affected by the systematic extinction, which lie within the limiting sphere for Mo $K\alpha$ radiation, 1186 were observed on layers $|l|=0$ to $|l|=20$ and their intensities recorded. Data for $00|l|$ reflections were obtained from this crystal by tipping the z axis 26° to the rotation axis.

It should be noted that these observations were made in the absence of any external electric field and only in a hemisphere of reciprocal space in which the sign of the index l was fixed. The former condition implies that the intensites are averages due to any domain structure which may be present; the latter is significant in view of the large imaginary component in the anomalous scattering of Mo $K\alpha$ radiation by lutetium (Dauben & Templeton, 1955).

Structure determination and refinement

The $LuMnO_3$ intensity data were corrected for Lorentz and polarization effects and for absorption. The latter corrections were made with the assumption of a cylindrical crystal having a linear absorption coefficient of 504·7 cm^{-1} for Mo $K\alpha$ radiation. Seven low-angle, high-intensity reflections were considered subject to extinction and a rough correction for this effect was applied (James, 1954).

A survey of the corrected intensities again drew attention to the regularity of the nonsystematic absences mentioned above. The requirement that these absences be predicted by any acceptable trial structure in fact eliminated the space group $P6c2$ (D_{3h}^2) from consideration before the orientation of the polar direction was known.

The relative weakness of reflections with $|l|$ odd suggested that a trial structure based on $P6_3cm$ would require placement of the rare-earth ions in the special positions 4(*b*) and/or 2(*a*) of that group.

* Based on Laue group 6/*mmm*. Further efforts to find intensity differences indicative of trigonal symmetry were inconclusive.

A Patterson projection using $h0\bar{h}|l|$ intensity data and a few preliminary structure factor calculations specifically indicated the following positions for Lu and Mn ions in $P6_3cm$:

$$\begin{gathered}4\ \text{Lu(1)}\ \text{in}\ 4(b)\text{: } (\tfrac{1}{3}, \tfrac{2}{3}, z)\ \textit{etc},\\ z=\tfrac{1}{4}+\varepsilon;\\ 2\ \text{Lu(2)}\ \text{in}\ 2(a)\text{: } (0,0,z;\ 0,0,\tfrac{1}{2}+z),\\ z=\tfrac{1}{4}-\varepsilon';\\ 6\ \text{Mn}\ \text{in}\ 6(c)\text{: } (x,0,z),\ \textit{etc},\\ x\simeq\tfrac{1}{3},\ z=0\,.\end{gathered}$$

Here the z parameter of Mn has been chosen to be zero arbitrarily and ε and ε' are about 0·02–0·03.

Since there is no contribution of rare-earth atoms to reflections with $|l|$ odd, the intensities of these reflections should be particularly sensitive to oxygen ion positions. With the restraint of the nonsystematic absences as a guide, the following oxygen positions were deduced:

$$\begin{gathered}6\ \text{O(1)}\ \text{in}\ 6(c)\text{: } (x,0,z),\ \textit{etc},\\ x\simeq\tfrac{1}{3},\ z\simeq\tfrac{1}{6};\\ 6\ \text{O(2)}\ \text{in}\ 6(c)\text{: } (x,0,z),\ \textit{etc},\\ x\simeq\tfrac{2}{3},\ z\simeq\tfrac{1}{3};\\ 4\ \text{O(3)}\ \text{in}\ 4(b)\text{: } (\tfrac{1}{3}, \tfrac{2}{3}, z),\ \textit{etc},\\ z\simeq 0;\\ 2\ \text{O(4)}\ \text{in}\ 2(a)\text{: } (0,0,z;\ 0,0,\tfrac{1}{2}+z)\,,\\ z\simeq\tfrac{1}{2}\,.\end{gathered}$$

Refinement of this trial structure was carried out by a series of structure factor and least-squares calculations. Observations were weighted according to the method given by Busing & Levy (1957), except for the seven reflections corrected for extinction which were arbitrarily given half their normal weight. The least-squares refinement was based on F^2, with a reliability factor R defined as

$$R=\Sigma|F_o^2-F_c^2|/\Sigma F_o^2\,.$$

Atom form factors for oxygen (doubly charged anion) were taken from Freeman (1959), those for manganese (triply charged cation) from Watson & Freeman (1961), and those for lutetium (triply charged cation) from Thomas & Umeda (1957). Corrections for the real component of the anomalous dispersion of Mo $K\alpha$ by lutetium were made with the f' value given by Dauben & Templeton (1955). The imaginary component of the anomalous dispersion correction is significant, but it was not introduced because (1) intensities of equivalent reflections with unlike signs of l could not be compared, and (2) $I(hk{\cdot}l)$ and $I(hk{\cdot}\bar{l})$ may be superimposed for each reflection, if the crystal studied contained domains oppositely oriented with respect to c. In this case, $F^2(hk{\cdot}l)$ and $F^2(hk{\cdot}\bar{l})$ should be computed (with imaginary anomalous dispersion

Table 3. *Atomic parameters for* $LuMnO_3$ *given by least-squares refinement based on the space group* $P6_3cm$

Atom	Position	X	Y	Z	β_{11}[1]	β_{22}	β_{33}	β_{12}[2]	β_{13}[3]	β_{23}[4]
Lu(1)	2(*a*)	0·0000[5]	0·0000[5]	0·2705	0·0032	0·0032	0·0018	0·0016	0·0000	0·0000
Lu(2)	4(*b*)	0·3333[5]	0·6667[5]	0·2266	0·0030	0·0030	0·0017	0·0015	0·0000	0·0000
Mn	6(*c*)	0·3212	0·0000[5]	0·0000[6]	0·0031	0·0041	0·0017	0·0020	−0·0005	0·0000
O(1)	6(*c*)	0·3071	0·0000[5]	0·1699	0·0036	negative	0·0010	negative	−0·0001	0·0000
O(2)	6(*c*)	0·6328	0·0000[5]	0·3397	0·0147	0·0233	0·0014	0·0117	−0·0006	0·0000
O(3)	2(*a*)	0·0000[5]	0·0000[5]	0·4836	0·0061	0·0061	0·0019	0·0031	0·0000	0·0000
O(4)	4(*b*)	0·3333[5]	0·6667[5]	0·0189	0·0019	0·0019	0·0035	0·0010	0·0000	0·0000

[1] $\beta_{11}=\beta_{22}$ for positions (*a*) and (*b*). [2] $\beta_{12}=\frac{1}{2}\beta_{22}$ for positions (*a*), (*b*), and (*c*). [3] $\beta_{13}=0$ for positions (*a*) and (*b*). [4] $\beta_{23}=0$ for positions (*a*), (*b*), and (*c*). [5] Parameter fixed by space group. [6] Arbitrarily fixed Z parameter.

Table 4. *Partial comparison of observed and calculated* $F^2(hk\cdot|l|)$

$hk\cdot\|l\|$	$F_o^2/100$	$F_c^2/100$	$hk\cdot\|l\|$	$F_o^2/100$	$F_c^2/100$	$hk\cdot\|l\|$	$F_o^2/100$	$F_c^2/100$	$hk\cdot\|l\|$	$F_o^2/100$	$F_c^2/100$
11,0	1110·9	1022·2	41,2	612·4	651·1	11,7	91·6	82·1	11,13	22·3	23·3
22,0	590·5	656·2	52,2	428·6	406·7	22,7	50·4	45·8	22,13	21·1	16·6
33,0	918·8	1034·1	63,2	119·1	121·5	33,7	0·0	0·0	41,13	16·1	12·5
44,0	325·9	281·2	74,2	162·5	157·2	44,7	18·0	12·1	51,13	0·0	1·0
55,0	191·6	172·2				21,7	0·0	1·2	52,13	15·9	7·6
66,0	201·8	200·1	11,3	18·9	18·6	31,7	0·0	0·5			
77,0	87·7	74·0	22,3	19·3	20·5	41,7	29·7	29·8	00,14	127·4	102·1
88,0	39·7	40·2	33,3	0·0	0·0	51,7	0·0	2·1	11,14	41·3	38·9
10,0	0·0	0·3	44,3	0·0	8·2	52,7	10·6	15·3	22,14	33·8	32·5
20,0	0·0	0·6	55,3	0·0	5·9				10,14	117·0	98·8
30,0	1781·3	2347·3	21,3	0·0	1·4	00,8	463·6	457·6	20,14	101·8	103·8
40,0	0·0	2·9	31,3	0·0	1·3	11,8	129·9	136·0	30,14	77·1	84·4
50,0	0·0	1·4	41,3	23·8	16·3	22,8	107·8	165·2			
60,0	683·7	787·6	51,3	0·0	1·2	10,8	232·7	228·6	11,15	5·8	3·8
70,0	0·0	3·8	52,3	16·1	10·7	20,8	182·4	179·0	22,15	4·1	3·5
80,0	0·0	1·4				30,8	320·8	325·2	21,15	0·0	1·3
90,0	341·7	306·5	00,4	1772·5	1858·1	40,8	164·9	161·8	31,15	0·0	1·7
			11,4	686·0	769·8				41,15	5·7	3·1
11,1	184·8	190·4	22,4	467·4	488·9	11,9	13·4	12·3			
22,1	96·8	85·0	33,4	587·4	624·4	22,9	14·0	10·3	00,16	47·0	45·2
33,1	0·0	0·0	44,4	216·9	193·9	33,9	0·0	0·0	11,16	72·5	85·5
44,1	18·2	16·6	55,4	135·4	124·3	44,9	6·4	5·1	22,16	64·7	73·1
55,1	0·0	7·9	66,4	152·0	144·2	21,9	0·0	0·5	10,16	37·6	41·1
66,1	0·0	0·1	10,4	113·0	115·5	31,9	0·0	0·5	20,16	37·9	42·6
21,1	0·0	3·1	20,4	137·5	134·5	41,9	10·7	8·4	30,16	34·5	37·8
31,1	0·0	1·3	30,4	929·9	1147·7	52,9	3·8	6·4			
41,1	56·1	48·2	40,4	62·1	55·1	63,9	0·0	0·0	11,17	10·2	9·9
51,1	0·0	3·2	50,4	82·2	72·4				22,17	8·1	8·1
61,1	0·0	1·0	60,4	482·1	495·3	00,10	56·8	46·4	21,17	0·0	0·4
71,1	2·8	12·8	70,4	26·4	24·0	11,10	105·9	97·8	31,17	0·0	0·2
81,1	0·0	2·9				22,10	83·6	78·2	41,17	4·1	6·9
52,1	27·5	21·6	11,5	113·5	113·9	10,10	253·7	240·8			
63,1	0·0	0·0	22,5	56·5	59·6	20,10	206·4	202·9	00,18	162·9	158·5
74,1	6·3	6·0	33,5	0·0	0·0	30,10	39·8	34·7	11,18	32·3	38·9
			44,5	23·5	14·7	40,10	178·9	173·4	22,18	33·9	34·7
00,2	840·3	687·1	55,5	14·8	7·2				10,18	17·6	20·5
11,2	1173·3	1297·9	21,5	0·0	2·3	11,11	36·1	32·2	20,18	15·5	19·3
22,2	719·3	869·2	31,5	0·0	1·1	22,11	22·5	22·6	30,18	104·8	131·7
33,2	276·1	243·7	41,5	45·5	37·2	33,11	0·0	0·0			
44,2	347·7	338·8	51,5	0·0	2·9	44,11	7·7	9·0	11,19	7·3	7·6
55,2	184·1	204·1	52,5	23·4	18·4	41,11	23·4	17·0	22,19	4·6	5·9
66,2	51·4	62·1				52,11	17·6	10·4	21,19	0·9	1·2
77,2	73·8	76·4	00,6	88·2	77·8				31,19	0·0	0·0
88,2	47·2	43·2	11,6	552·1	681·4	00,12	98·6	72·4	41,19	8·5	4·7
10,2	62·8	49·0	22,6	433·0	464·7	11,12	55·9	59·2			
20,2	74·5	66·4	33,6	66·5	60·4	22,12	48·7	45·1	00,20	58·8	40·3
30,2	401·0	398·8	44,6	204·9	175·5	10,12	165·8	139·3	11,20	54·9	77·5
40,2	22·4	18·9	55,6	131·3	112·4	20,12	148·7	131·2	22,20	56·8	67·5
50,2	37·1	28·9	66,6	32·1	22·3	30,12	73·0	54·4	10,20	3·3	4·3
60,2	220·3	200·7	10,6	279·1	260·7	40,12	99·0	101·2	20,20	3·3	2·8
70,2	0·0	9·3							30,20	25·8	35·3

corrections) and averaged before comparison with the observed $F^2(hk\cdot|l|)$. In any case, the difference between the computed average $[F^2(hk\cdot l)+F^2(hk\cdot\bar{l})]$ and $F^2(hk\cdot|l|)$ calculated with only a real dispersion correction was considered small, and the imaginary correction was therefore omitted. Refinement began

with a single, isotropic temperature factor and was later modified to include anisotropic temperature factors for individual atoms (Levy, 1956). The iterative computations were carried out on an IBM 704 with a program written by Busing & Levy (1959).

Convergence from an initial R value of 0·33 to a final value of 0·13 was obtained within five refinement cycles. Despite this satisfactory agreement factor, the final atom parameters could not be accepted as definitive because of the unacceptable values assumed by components of the temperature factors of O(1) and O(2). Table 3 lists the atom positions and temperature factors from the penultimate least-squares cycle. Probable errors are not given since their significance is doubtful.

Several possible reasons for the temperature factor anomalies may be proposed. The first is an interaction between parameters in the least-squares refinement. This effect has been discussed by Evans (1952), Shirane, Pepinsky & Frazer (1956), and most recently by Geller (1961). The correlation matrix was computed and, as might be expected, large coefficients ($>0·5$) relating the z coordinates of pairs of atoms were found. While this calculation suggested that the structure of $LuMnO_3$, like that of $BaTiO_3$, may be essentially indeterminate from X-ray diffraction data, it did not show any direct cause for the behavior of the temperature factors of O(1) and O(2).

Another reason, related to the first, could be an incorrect anomalous-dispersion correction. Templeton (1955) has discussed the large effect on temperature and scale parameters to be expected if this correction is not properly made. The particular problems encountered in the application of dispersion corrections for $LuMnO_3$ have been outlined above.

A third cause for the anomalies may be an incorrect assignment of crystal symmetry. Efforts to distinguish between the possible space groups $P6_3cm$ and $P3c1$ have been described. Should the planes on which O(1) and O(2) lie in $P6_3cm$ be only pseudomirrors, the constraint imposed by enforced mirror symmetry might lead to the observed temperature factor effect for O(2). The effect for O(1) would remain unexplained, however.

Table 4 gives a partial list of observed $F^2(hk\cdot|l|)$ and those computed from the input parameters of the last least-squares cycle. Atom parameters used in the calculation are the same as in Table 3, except for β_{22} of O(1) which was arbitrarily taken to be +0·00002.

Discussion

Because of the possible indeterminacy of the refinement, the atom parameters listed in Table 3 must be considered as approximative. This approximate structure will be discussed with the reservation that future work may alter, or add, details.

A general view of the structure is shown in Fig. 1 and a list of close interionic contacts is given in Table 5. These distances should also be treated as indications of the true separations. The structure may be considered in terms of an *ABCACB* stacking sequence (normal to z) of layers of hexagonally coordinated oxygen ions in which every *A* layer contains a manganese ion at about the center of every other equilateral triangle of oxygens ions. Oxygen ions in a given layer are not close packed [d(O–O)= 3·5 Å compared with $2R$(O–O)=2·8 Å], but O–O contacts between layers are minimal; the net interlayer separation is therefore smaller than that in hexagonal $BaTiO_3$ (Burbank & Evans, 1948) where an *ABCACB* stacking of close-packed layers is reported.

There is a fivefold coordination of oxygen ions about each manganese ion and the coordination polyhedron approximates a trigonal dipyramid. The dipyramids share midplane corners, but not apices. This type of coordination has been described for molecular PCl_5 (Brockway & Beach, 1938) and other

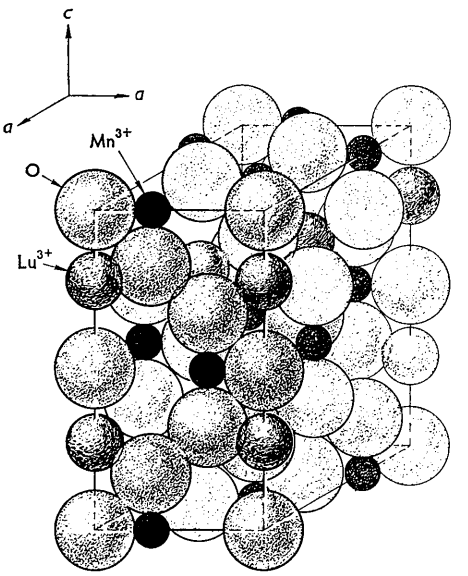

Fig. 1. The approximate ionic arrangement in a unit cell of $LuMnO_3$.

Table 5. *Interionic contacts in* $LuMnO_3$

Atoms	Separation	Atoms	Separation
Mn–O(2)	1·84 Å	(2) O(1)–O(1)	3·22 Å
Mn–O(1)	1·93	(4) O(1)–O(1)	3·63
Mn–O(4)	1·98	O(1)–O(2)	2·76
(2) Mn–O(3)	2·06	(2) O(2)–O(2)	2·83
		O(1)–O(3)	2·82
(3) Lu(1)–O(1)	2·18	(2) O(1)–O(4)	2·70
(3) Lu(1)–O(2)	2·35		
Lu(1)–O(3)	2·42	(4) O(2)–O(2)	3·32
		(2) O(2)–O(2)	3·84
(3) Lu(2)–O(1)	2·19	O(2)–O(3)	2·75
(3) Lu(2)–O(2)	2·31	(2) O(2)–O(4)	2·81
Lu(2)–O(4)	2·36		
		(6) O(3)–O(4)	3·51
		(3) O(4)–O(4)	3·49

covalent compounds of Group V elements; its occurrence in a three-dimensional framework is unusual, but an instance may be found in $BaO.6Fe_2O_3$ (Adelsköld, 1938; Berry, 1951; Bertaut, Deschamps, Pauthenet & Pickart, 1959).

The coordination of oxygen ions about each rare-earth ion is sevenfold if the oxygen atom directly above (along 6_3) or below (along 3) the rare-earth ion is included in the coordination group. The arrangement is similar to that in the hexagonal rare-earth oxides, but with three short and four long R–O contacts in each group. If the distances in Table 5 are accepted, the relative orientations of long and short contacts are different about Lu(1) and Lu(2).

Further discussion of detailed interionic distances and angles would seem to be out of place in view of the uncertainties in the refinement of the X-ray diffraction data.

Finally, one may speculate on the reasons for the existence of this unusual structure. The decreasing size of the lanthanide series cations with increasing atomic number should decrease the stability of a perovskite-type lattice. The critical dependence on lanthanide ion size is reflected in the existence of a perovskite-type polymorph of $YMnO_3[R(Y^{3+})=1{\cdot}06$ Å] and the absence of such polymorphs for manganese (III) trioxides with smaller rare-earth ions.*

ABO_3 iron (III) trioxides of all lanthanides up to and including lutetium have been reported to possess a distorted perovskite lattice (Forrat, 1958; Sherwood, Remeika & Williams, 1959; Geller, 1956; and Geller & Wood, 1956). Therefore, despite the effect of lanthanide ion size, the ability of trivalent manganese to adopt a fivefold trigonal dipyramid coordination must be considered as the prime reason for the stability of the structure. This coordination arrangement suggests covalent character in the Mn–O bonds, which, in the valence-bond description, would utilize the dsp^3 hybrid bonding orbitals of Mn^{3+} (Kimball, 1940). This simple valence-bond picture would indicate a high-spin configuration for the manganese ion.

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* Diffraction patterns of polycrystalline $ErMnO_3$ have been obtained at temperatures up to 800 °C in a Unicam S. 150 high-temperature X-ray diffraction camera. No indication of a transformation to a perovskite-type structure was found.

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